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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C10G 32/02

A1

(11) International Publication Number: **WO 95/30726**

(43) International Publication Date: 16 November 1995 (16.11.95)

(21) International Application Number: PCT/US95/05869

(22) International Filing Date: 10 May 1995 (10.05.95)

(30) Priority Data:

08/240,308	10 May 1994 (10.05.94)	US
08/418,324	7 April 1995 (07.04.95)	US

(81) Designated States: AU, CA, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

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(54) Title: ELECTROFLOCCULATOR FOR SOLIDS REMOVAL IN HYDROCARBON PROCESSES

(57) Abstract

The instant invention is directed to a method for removing catalyst particles, having at least about 0.1 wt. % metal in the zero valence state, from hydrocarbon process fluids using an electric field. The invention is further directed to an improved reactor apparatus wherein a hydrocarbon process vessel is attached to an electroflocculating apparatus.

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ELECTROFLOCCULATOR FOR SOLIDS REMOVAL IN HYDROCARBON PROCESSES

Field of the Invention

The present invention is directed to a continuous method of removing solid catalyst particles from hydrocarbon process fluids, including Fischer-Tropsch process fluids, using an electric field preferably an electric field generated by an electroflocculating apparatus. The invention is further directed to such apparatus.

Background of the Invention

In most chemical processes involving solid catalyst particles dispersed in a liquid, an easy separation method for removing the catalyst particles from the liquid is considered critical. Despite the fact that smaller catalyst particles can promote higher reactor productivity and product selectivity, larger particles are used to avoid the problems encountered in separating small catalyst particles or in confining particles in the process vessel using conventional filtration or settling techniques.

Summary of the Invention

Thus, one aspect of the instant invention advantageously allows catalyst free product fluid to be removed from a process without the use of filters which become blinded (clogged) necessitating interrupting the process for filter replacement or cleaning. Applicants have discovered a way of separating particles from process fluids. The method of the instant invention has no effect on the catalyst surface area, particle density, particle size, or catalyst activity.

The instant invention is directed to a method for separating solid catalyst particles from hydrocarbon process fluids comprising the steps of:

(a) introducing a mixture of a process fluid and solid catalyst particles, said solid catalyst particles containing at least about 0.1 wt.% metal in the zero valence state, and wherein said process fluid exhibits an electric conductivity less than about 1×10^{-10} ohm^{-1} m^{-1} into an electric field, wherein said electric field has an electric field strength of greater than 100 volts/cm and a frequency of about 0.1 hertz to about 5000 hertz, to produce agglomerated solid catalyst particles;

(b) separating, through gravity, said agglomerated solid catalyst particles from said hydrocarbon process fluid.

In a preferred embodiment of the invention, the process further comprises step:

(c) removing said separated agglomerated solid catalyst particles from said electric field to produce deagglomerated solid catalyst particles.

In an even more preferred embodiment, the process further comprises step:

(d) reintroducing said deagglomerated solid catalyst particles into the hydrocarbon process reaction zone. Thus, in a preferred embodiment a recirculating process can be conducted.

The invention is further directed to an improved apparatus for the continuous removal of solid catalyst particles containing at least 0.1 wt.% metal in the zero valence state, from process fluids following reaction wherein the improvement comprises attaching a hydrocarbon process vessel to an

electroflocculating apparatus, said electroflocculating apparatus comprising:

(a) a hollow shell having at least one inlet for acceptance of a mixture of process fluids and solid catalyst particles, said catalyst particles containing at least 0.1 wt.% metal in the zero valence state, a top outlet for drawing off process fluids having solid catalyst particles removed therefrom, and a bottom outlet for expelling deagglomerated catalyst particles;

(b) a plurality of electrodes in functional relation with said hollow shell, wherein said electrodes extend above said hollow shell inlet and;

(c) a high voltage power source coupled to said electrodes and capable of producing an electric field strength of greater than 100 volts/cm and a frequency of about 0.1 to about 5000 hertz within said hollow shell:

Hence, it can be seen that the apparatus allows for the continuous removal of solid catalyst particles from process fluids and conveyance of the removed solid catalyst particles, which deagglomerate once removed from the electric field back into the reaction zone, if desired. The electroflocculator can be located within or without (outside) the reactor.

Brief Description of the Drawings

Figure 1 depicts one possible electroflocculating apparatus where the electroflocculator is located inside a hydrocarbon synthesis bubble column.

Figure 2 shows another possible electroflocculator set up.

Detailed Description of the Invention

The instant invention teaches a method for separating catalyst particles from process fluids having such particles suspended therein. The method is capable of separating particles which are 1 micron in size up to and including a 0.3 cm particles. The invention can remove suspended particles from any type of hydrocarbon liquid. The invention is particularly useful for removing catalyst particles from slurry process fluids, particularly bubble column slurry process fluids, ebulating bed processes and stirred process fluids. Advantageously, catalyst particles can be separated from the process fluids in accordance with the instant invention without any pretreatment of the process fluids. Thus, they can be introduced directly into the electroflocculator aparatus from the hydrocarbon reaction vessel.

The invention merely requires that the solid catalyst particles contain at least 0.1 wt.%, based on the total particle weight, of a metal in its zero valence state.

Applicants have discovered that applying an electric field to a process fluid which contains about 0.1 to 50 wt.%, preferably 0.3 to 50 wt.% suspended solid catalyst particles containing at least 0.1 wt.% metal in the zero valence state, causes the solid catalyst particles to be temporarily agglomerated, causing them to settle, through gravity, out of the process fluid enabling the ready removal of process fluid from the fluid/solid mixture. Once the catalyst particles have settled and passed out of the electric field, they deagglomerate to their original size and are usable once again. Hence, they can be immediately returned to the reaction zone without interruption of the process being performed and a recirculating process (which reutilizes the deagglomerated catalyst particles) can be conducted. Thus, the present invention can be utilized to reclaim, e.g., supported Fischer-Tropsch catalysts from slurry

Fischer-Tropsch media. The invention can additionally be used on promoted cobalt catalyst such as rhenium promoted cobalt. For example, the invention can be used to separate a cobalt-rhenium on titania catalyst from Fischer-Tropsch media. The above catalysts are merely illustrative and are not meant to be limiting. The instant invention is capable of removing >95% of the solid catalyst particles directly from the process fluid without the aid of any pretreatment steps.

For illustration, a slurry process fluid can be passed through an electroflocculator, in accordance with the instant invention, whereupon the catalyst particles present will agglomerate and settle to the electroflocculator vessel bottom. Once the catalyst particles are outside of the forces of the electrical field, they deagglomerate. The catalyst particles can then be passed back into the slurry process reaction zone if desired. Process fluid having catalyst particles removed therefrom can be withdrawn from the electroflocculator vessel by any suitable means. In the instant process there is substantially no migration of the catalyst to the electrodes, preferably no such migration will occur.

In an ebulating bed process where liquid is used to fluidize the catalyst, small catalyst fragments entrained from the catalyst bed into the process fluid can likewise be removed and clarified liquid return to the ebulating bed vessel. In this manner, fragments of catalyst particles will not be present in fluid above the ebulating bed and will thus prevent pump clogging when the liquid is recirculated.

The preferred mode of carrying out the instant invention is to pass the process fluid having suspended solid catalyst particle therein through an electroflocculator by utilizing techniques such as the "downcomer" effect commonly practiced in chemical engineering. The flocculator is a vessel equipped with an AC voltage source across two electrodes (hot and ground) capable of producing AC voltage of from about 0.1 hertz, up to and

including about 5000 hertz of current. The electrical field strength produced will be from about 100 volts/cm up to and including about 100,000 volts/cm, preferably from about 200 to about 50,000 volts/cm.

If the process is being conducted in a hydrocarbon synthesis bubble column, the electroflocculator will be equipped with a metal screen, at the area where the process fluid and catalyst particles enter to exclude gas bubbles. The openings of the screen should be adequate to exclude most gas bubbles in the process fluid but allow the passing of the particles. More preferably, the electroflocculator will be equipped with both a baffle and a metal screen. The baffle helps to further exclude gas bubbles. Once the solid catalyst particles experience the electric field, they agglomerate and settle through the opening at the bottom of the electroflocculator. They can thus be readily removed. The departiculated process stream can be collected by any suitable means such as siphoning from near the top of the electroflocculator, decanting, etc.

The instant method can be carried out with an electroflocculator inside the reaction vessel, enabling the agglomerated catalyst particles, which deagglomerate without any change in size, surface area, particle density or catalyst activity, to be passed back into the reaction zone once removed from the electroflocculator. The electroflocculator could alternatively be external to the reaction vessel itself. In the external setup, the deagglomerated particles may be returned to the reaction zone by any suitable means such as pumping.

Applicants believe that once the process fluid/solid catalyst particle mixture enters the electric field, the small catalyst particles, having zero valence metal therein, will experience electric dipole/dipole interactions and will flocculate to agglomerates that exhibit a much higher settling velocity than deagglomerated particles. Because gas will have preferably been removed from the fluid, there will be a driving force for the

liquid to flow downward due to the Downcomer effect. This Downcomer effect will be countered by any process fluid removal during settling. Provided the net rising velocity of the process liquid is less than the settling velocity of the agglomerated particles, most particles can be removed through enhanced settling of the agglomerates. If desired, the electroflocculator may be equipped with a screen or filter at the product withdrawal outlet to filter any solid residual catalyst particles that might be present near the siphoning outlet due to inadequate residence times.

The horizontal cross-sectional area of the upper zone of the electroflocculator, the zone of high electric field above the entrance and below the exit port for clarified product, will be sized such that the liquid upflow velocity in this zone is about a factor of 2 to about 40 of the Stokes velocity of the particles being separated. The higher the electric field used, as well as the zero valence metal content of the particles, the higher the factor that can be used. The height of this zone should be such that it allows a residence time of at least 0.1 minutes, preferably at least about 0.5 minutes. The longer the residence time, the greater the departiculation efficiency.

The apparatus which will preferably be used to carry out the method of the instant invention will consist of a reactor vessel equipped with an electroflocculator attached to the outside of the reactor or present within the reactor. Additionally, the electrodes of the electroflocculator may be within or external to the flocculator shell. The electrodes need only produce an electric field which penetrates the process fluid having suspended catalyst particles therein, they needn't directly contact the fluid. The electroflocculator on the outside of the reactor vessel will be piped to the reactor and will contain a valve for process fluid drawoff. The bottom of the flocculator will be piped back into the reactor to enable the agglomerated catalyst particles to be removed from the electric field, deagglomerated and passed back into the reactor to participate in the reaction

being carried out if a recirculating process is desired.

When the electroflocculator is contained within the reactor, its vessel walls will preferably have a portion composed of wire mesh of about 200-2000 micron opening size, which will allow the slurry process fluid to flow into the electro-flocculator. The bottom of the flocculator will be open, allowing agglomerated particles to pass out of the flocculator and into the process vessel. A portion of the flocculator, preferably the top, will protrude from the reactor vessel, enabling process fluid having catalyst removed therefrom to be siphoned off. However, if, e.g. an ebulating bed system is being used, the process fluid withdrawal port will be inside the process vessel allowing liquid to be returned to the reaction zone.

In a nonlimiting embodiment of the electroflocculator apparatus, the electroflocculator is located inside a hydrocarbon synthesis bubble column reactor. It consists of a hollow metal shell (A) which serves as a ground electrode, a center electrode (B) connected to a high voltage source (C) which electrode is insulated from the shell (A). Slurry process fluid enters through ports (D) which are metal screens and serve also as grounded grid electrodes. The bottom of the shell is open (E) to the reactor to allow for deagglomerated particles to be expelled from the shell. The top of the shell is connected to a tube (F) which serves as a drawoff port for the removal of product fluid. The efficiency of the cylinder has been increased by the addition of a baffle plate (G) external to the shell beneath the screen. The baffle prevents gas bubbles from contacting the screen. Removal of gas bubbles sets up a gradient which promotes the continuous flow of slurry from the reactor into the shell and exit through the opening (E) due to the Downcomer effect.

In another nonlimiting embodiment of the apparatus, the system comprises a shell (A) equipped with an electrode pair consisting of a metal rod (B) connected to a high voltage source (D) and a metal mesh screen (C) connected to the ground. A

recirculating pump (H) is used to pump feed to the electro-flocculator through port (E). Concentrated slurry exits the flocculator via exit port (F) and is then recirculated via the pump. Departiculated raffinate is withdrawn via port (G).

The above setups are merely illustrative, not limiting.

The process fluids which are clarified by use of the instant invention have a dielectric constant of about 2 to about 4, preferably about 2 to about 3. They exhibit an electric conductivity less than about 1×10^{-10} ohm^{-1} m^{-1}, preferably less than 5×10^{-11} ohm^{-1} m^{-1}.

The following examples are for illustration and are not meant to be limiting.

The experiments were carried out in a 1 7/8" ID by 5.5" long glass vessel fitted with an electrode pair consisting of a 1.7"D x 3"L cylindrical metal screen and a central electrode. The electrodes were connected to the terminals of a high voltage power source capable of generating up to 10 thousand volts of electric potential at frequencies ranging from 40 hertz to 250 hertz.

Slurries of solid particles of 63 micron cobalt on porous TiO_2 particles with ~0.3 cc/gm pore volume with Co in its zero valence and containing about 11.5 wt.% of the above catalyst or 22 microns of conventional Fischer-Tropsch iron catalyst dispersed in hydrocarbon oil were loaded to the surge vessel and pumped through the electroflocculator described above. It was found that whenever a voltage between 2000 and 4000 volts/cm electric field with frequency between about 40 hertz to about 250 hertz was applied to the electrodes, the effluent stream from the vessel turned in color from dark to clear, indicating a significant reduction of solids content in the stream. In fact, as shown in Table 1, the analysis of the solids content in tests at 4000 volts/cm electric field and about 200 hertz indicated that

the electric field in the electroflocculator reduced the solids in the stream by 93 to 97%.

The experiments show that in this case the electroflocculator was capable of removing fine particles from a slurry of a nonaqueous nonelectrolitic liquid with electrical conductivity of 2 x 10^{-13} ohm^{-1} m^{-1} and dielectric constant of 2.02.

TABLE 1

RESULTS OF ELECTROFLOCCULATION DEPARTICULATION
TESTS WITH CATALYST IN HYDROCARBON LIQUID*

Test	Catalyst Type	Flow Rate cc/Min.	Solids in Raffinate when High Volt. On Gm/cc	Solids in Raffinate when High Volt. Off Gm/cc	% Solids Removal
A	Co/Re on TiO2** Dp = 63 μ	480	Less than 0.0040	0.0625	Greater than 93.6
B	Co/Re on TiO2** Dp = 63 μ	250	Less than 0.0048	0.1680	Greater than 97.2
C	Conventional Fischer-Tropsch Iron Catalyst (Fe; Cu; K; Si) Dp = 22 μ	140	Less than 0.0028	0.0531	Greater than 94.8

* Hydrocarbon oil of viscosity ~1.8 cP
** Activated and passified
Dp = Mean particle size

A second series of experiments were carried out in an apparatus shown in Figure 2 which was designed to simulate the operation of which was designed to simulate the operation of an electroflocculator to confine catalyst in a chemical reactor. A 1 7/8" ID by 5.5" high glass vessel was fitted with an electrode pair consisting of a 1.7"D x 3"L cylindrical metal screen and a central electrode. They were connected to the terminals of a high voltage power source capable of generating up to 10 thousand volts, producing an electric field of 2000 to 4000 volts/cm at frequencies from 50 to 250 hertz. Slurry was fed from a pump into the side of the electroflocculator vessel close to the bottom of the electrode pair at a flow rate of about 1300 cc/min. The solid particles were to be electroflocculated in the zone between the two electrodes, settled to the bottom of the vessel, and removed as a concentrated slurry at flow rates from 840 to 1080 cc/min. The raffinate with solids removed exited from the top of the vessel at flow rates from 280 to 420 cc/min. In the lab test, the returned concentrated slurry and raffinate streams were remixed to reconstitute the feed for a continuous test to reach steady state.

Batches of slurries of catalysts in hydrocarbon oil with mean particle size of 63 microns and 22 microns were tested at 10 KV and 200 hertz. The results are listed in Table 2. At a flow rate of about 1300 cc/min. of the raffinate stream departiculation efficiencies from 95% to 99.5% were achieved.

To demonstrate that electroflocculation can also be carried out using electrodes insulated from the slurry, a small batch electroflocculation test tube was set up to allow a visual confirmation of the flocculation when the electric voltage was applied to the slurry. In this unit, two aluminum foil electrodes were attached to the outside of the glass tube, and connected to the 10 KV/200 hertz voltage source. In separate tests using conventional Fischer-Tropsch Iron Catalyst (Fe; Cu; K; Si) of 22 micron size and 50 micron particles of 5% platinum on the surface

of alumina each suspended in hydrocarbon liquid as test samples, oth solids were observed to flocculate in the liquid when the high voltage was turned on and deflocculate when the voltage was turned off. Apparently, the electric field can penetrate the glass wall of the test tube and flocculate the solids. Thus, electro-flocculation can also proceed with insulated electrodes.

TABLE 2

RESULTS OF ELECTROFLOCCULATION DEPARTICULATION

Test	Catalyst Type	Feed Stream Solids Conc. Gm/cc	Feed Stream Flow Rate cc/Min.	Raffinate Stream Solids Conc. Gm/cc	Raffinate Stream Flow Rate cc/Min.	Concentrated Slurry Stream Solids Conc. Gm/cc	Concentrated Slurry Stream Flow Rate cc/Min.	Departiculation Efficiency %
D	Co/Re on TiO2** Dp = 63 μ	0.40	1260	0.0022	420	0.60	840	99.5
E	Co/Re on TiO2** Dp = 22 μ	0.21	1340	0.0019	280	0.27	1060	99.1
F	Co/Re on TiO2** Dp = 22 μ	0.21	1370	0.0097	420	0.30	950	95.4

* At 10 KV/-200 Hz
** Activated and passified
Dp = mean particle size

CLAIMS:

1. A method for separating solid catalyst particles from hydrocarbon process fluids comprising the steps of:

(a) introducing a mixture of a process fluid and solid catalyst particles, said solid catalyst particles containing at least about 0.1 wt.% metal in the zero valence state, wherein said process fluid exhibits an electric conductivity less than about 1 x 10^{-10} ohm^{-1} m^{-1}, into an electric field, wherein said electric field has an electric field strength of greater than 100 volts/cm and a frequency of at least about 0.1 hertz and to produce agglomerated solid catalyst particles;

(b) separating, through gravity, said agglomerated solid catalyst particles from said hydrocarbon process fluid.

2. A method according to claim 1, further comprising step (c), removing said separated agglomerated solid catalyst particles from said electric field to produce deagglomerated solid catalyst particles.

3. A method according to claim 2, further comprising step (d), reintroducing said deagglomerated solid catalyst particles into a hydrocarbon process reaction zone.

4. A method according to claim 1 wherein said solid catalyst particles are 1μ to 0.3 cm particles.

5. A method according to claim 1 wherein said mixture of a process fluid and solid catlayst particles contains about .1 to about 50 wt.% of solid catalyst particles.

6. A method according to claim 1 wherein said mixture of process fluid and solid catalyst particles is introduced directly into said electric field without any pretreatment.

7. A method according to claim 1 wherein said method removes >95% of said solid catalyst particles from said mixture of process fluid and solid catalyst particles.

8. An improved reactor apparatus for the continuous removal of solid catalyst particles containing at least 0.1 wt.% metal in the zero valence state, from slurry process fluids following reaction wherein the improvement comprises attaching a hydrocarbon process vessel to an electroflocculating apparatus, said electroflocculating apparatus comprising:

(a) a hollow shell having at least one inlet for acceptance of a mixture of hydrocarbon process fluids and solid catalyst particles, said catalyst particles containing at least 0.1 wt.% metal in the zero valence state, a top outlet for drawing off product and a bottom outlet for expelling deagglomerated catalyst particles;

(b) a plurality of electrodes in functional relation with said hollow shell, wherein said electrodes extend above said hollow shell inlet and;

(c) a high voltage power source coupled to said electrodes and capable of producing an electric field strength of greater than 100 volts/cm and a frequency of about 0.1 to about 5000 hertz within said hollow shell.

9. An apparatus according to claim 8 wherein said electroflocculator is located within or without the reactor.

10. A method according to claim 1 wherein said process fluid is a slurry, ebulating bed or stirred process fluid.

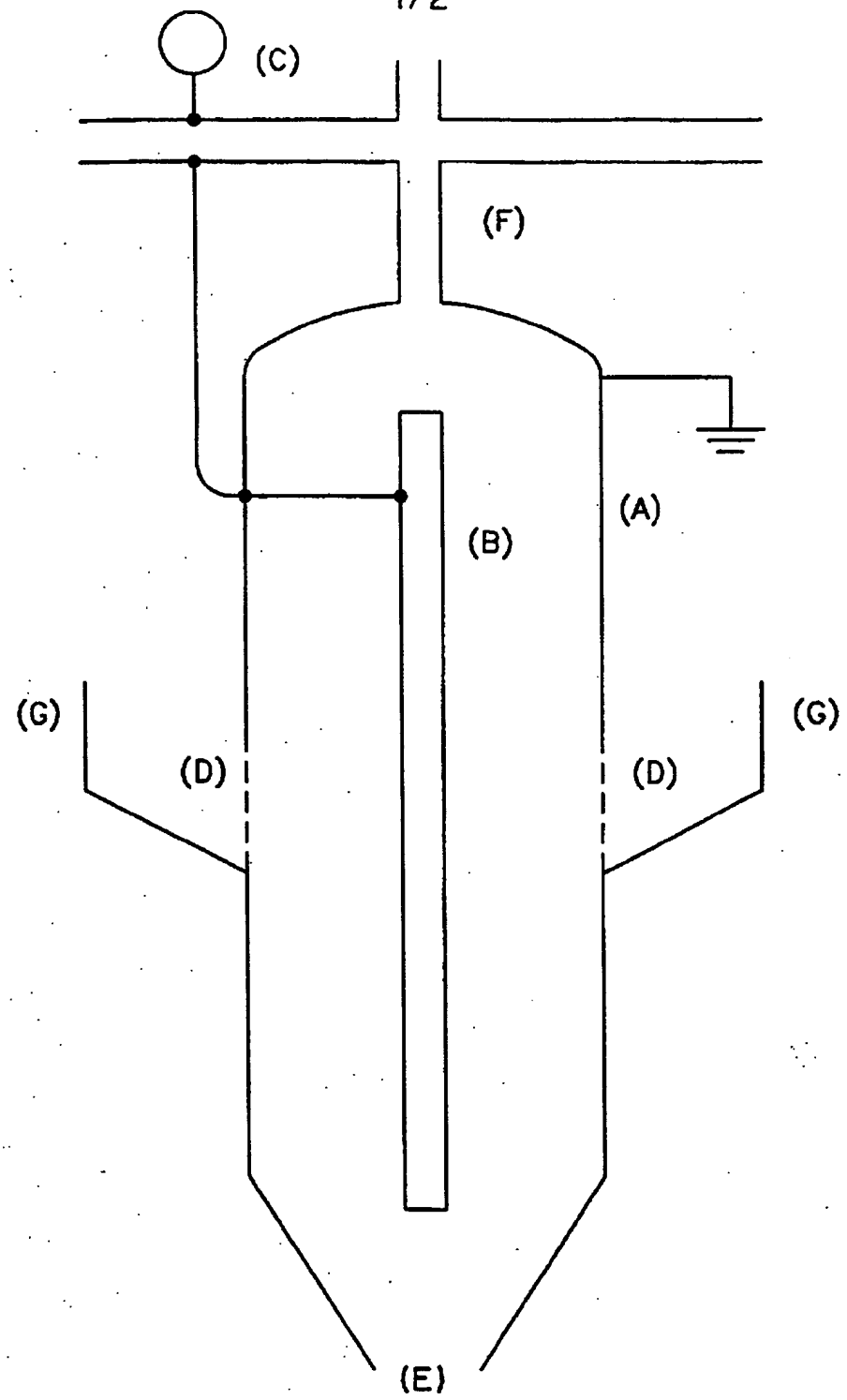

FIG. 1

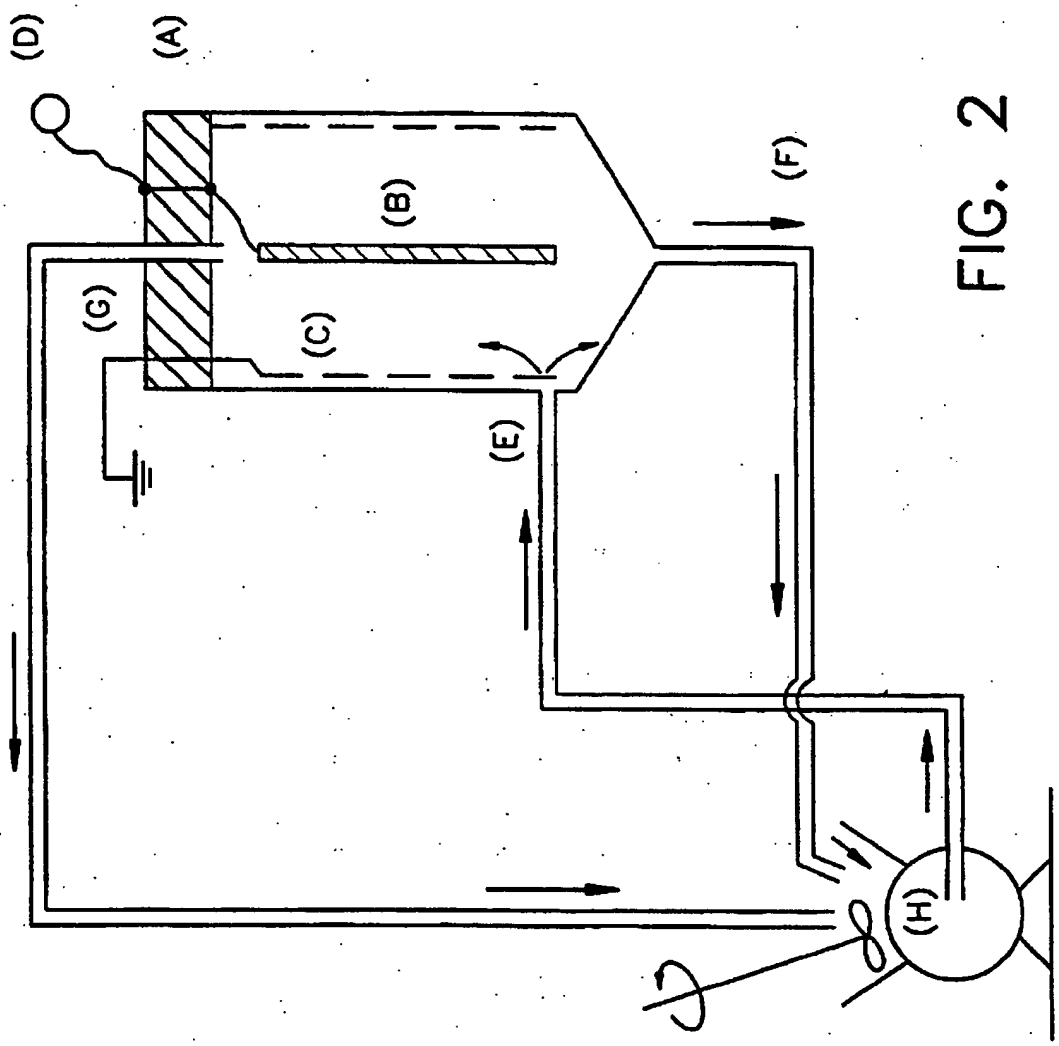

FIG. 2

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 95/05869

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G32/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,85 03017 (AMERICAN FILTRONA CORPORATION) 18 July 1985 see page 14, line 1; claims 1-22	1-10
A	US,A,3 928 158 (GULF) 23 December 1975 see the whole document	1-10
A	US,A,4 358 379 (INOUE) 9 November 1982	
A	EP,A,0 570 108 (GENERAL ATOMICS) 18 November 1993	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 September 1995	18 -09- 1995

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Michiels, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int[illegible]l Application No
PCT/US 95/05869

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-8503017	18-07-85	US-A-	4579637	01-04-86
		AU-A-	3836685	30-07-85
		CA-A-	1240953	23-08-88
		EP-A-	0167619	15-01-86
US-A-3928158	23-12-75	NONE		
US-A-4358379	09-11-82	NONE		
EP-A-570108	18-11-93	US-A-	5308586	03-05-94
		JP-A-	6007705	18-01-94

PATENT COOPERATION TREATY

PATENTS
DATE RECEIVED 13 OCT 2004

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
SCHLUMBERGER CAMBRIDGE RESEARCH LTD 3375
Intellectual Property Law Dept. AKM
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High Cross
Madingley Road
Cambridge CB3 0EL
UNITED KINGDOM

AMEND CLAIMS
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13.10.04
13.10.04

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

WRITTEN OPINION
DEADLINE: 13 JAN 05
Photocopy
13.10.04
13.10.04

Applicant's or agent's file reference 57.0551 WO PCT	Date of mailing (day/month/year) 13/10/2004
	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/GB2004/002863	International filing date (day/month/year) 02/07/2004
Applicant M-I L.L.C.	

1. [x] The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

   When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

   Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes 1211 Geneva 20, Switzerland, Fascimile No.: (41-22) 740.14.35

   For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

   [ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

   [ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

   Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

   The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

   Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until **30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

   In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

   See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Chrystalla Louca-Dreher

Form PCT/ISA/220 (January 2004) *(See notes on accompanying sheet)*

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by canceling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped),whether

(i) the claim is unchanged;

(ii) the claim is cancelled;

(iii) the claim is new;

(iv) the claim replaces one or more claims as filed;

(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."

2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."

3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."

4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international appplication is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

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